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CORRELATION OF THERMODYNAMIC STABILITIES OF CHARGE TRANSFER COMPLEXES OF ANTHRACENE AND CHLORANIL WITH THOSE OF TETRA-CYANOETHYLENE

M. Lotfi
Department of Chemistry, University of Mashad, Mashad, Iran
and
R. M. G. Roberts*
Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex, CO4 4SQ England

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Abstract—The formation constants of charge-transfer complexes of a number of 9- and 9,10-substituted anthracenes with chloranil have been measured by a spectrophotometric method and the corresponding thermodynamic parameters ΔG°_c, ΔH°_c and ΔS°_c evaluated in various solvents. $\bar{\nu}_{max}$ values of the charge-transfer band for chloranil were linearly related to those for tetracyanoethylene (TCNE). Good correlations were also obtained between $\bar{\nu}_{max}$ and the corresponding ionisation potentials Ip of the donor molecules. In addition ΔG°_c varied linearly with Ip and from these correlations, values of ΔG°_c, etc. for the corresponding TCNE complexes could be calculated. These values are otherwise very difficult to obtain due to the high reactivity of TCNE.

Charge transfer complexes have been postulated as intermediates in a great number of reactions[1] but often it is difficult to assess their mechanistic importance. A case in point is the Diels–Alder reaction where transient coloured species have been described as charge transfer complexes and have been invoked as reaction intermediates. Until very recently their role in the reaction has been uncertain. Two mechanistic pathways are possible, one involving the complex as a true intermediate (Scheme 1) and the other in which complex formation is a side reaction (Scheme 2).

$$A + B \overset{K_c}{\rightleftharpoons} C_T \xrightarrow{k_1} \text{product} \qquad (1)$$

Scheme 1

$$C_T \overset{K_c}{\rightleftharpoons} A + B \xrightarrow{k_2} \text{product.} \qquad (2)$$

Scheme 2

It can be readily shown that under conditions where one of the reagents is in a large excess, Scheme 1 yields the equation

$$k_{exp} = \frac{K_c k_1}{1 + K_c[B]} \qquad (3)$$

and Scheme 2 gives

$$k_{exp} = \frac{k_2}{1 + K_c[B]}. \qquad (4)$$

Furthermore, if $K_c[B] \ll 1$, then (3) and (4) reduce to $k_{exp} = K_c k_1$ and $k_{exp} = k_2$ respectively.

Thus the observed enthalpy of activation will be dependent on the enthalpy of complex formation (ΔH°) for (1) but will be independent of ΔH° for (2).

$$\text{i.e.} \qquad \Delta H^{\neq}_{obs} = \Delta H_1^{\neq} + \Delta H^\circ \qquad (5)$$

where $\Delta H_1^{\neq}$ is the activation enthalpy for conversion of complex into products. If ΔHo is sufficiently negative then negative values of $\Delta H^{\neq}_{obs}$ could be envisaged. Kiselev and Miller[2] have studied the kinetics of the Diels–Alder addition of tetracyanoethylene (ethenetetracarbonitrile, TCNE) to 9,10-dimethyl anthracene and found the sought-after negative $\Delta H^{\neq}_{exp}$ values in a variety of solvents. This strongly supports the postulate that the charge-transfer complexes lie along the reaction coordinate in the Diels–Alder reaction. In view of their mechanistic importance, it was decided to investigate the thermodynamic stability of these complexes in the anthracene series.

Since TCNE reacts very rapidly with all but the most deactivated anthracenes (e.g. 9-bromo and 9,10-dibromoanthracene), the determination of the thermodynamic parameters for complex formation is extremely difficult. However, complexes with chloranil are kinetically stable and hence the parameters for TCNE could, in principle, be obtained by various correlation procedures. Thus, the charge transfer complexes of a series of 9-substituted anthracenes with TCNE were investigated using the usual UV spectroscopic methods. The choice of solvent in this study is important since many solvents compete with the donor species in the formation of complexes (not necessarily of the charge-transfer type). Prausnitz *et al.*[3,4] have reported values of the association constants for various aromatic donor-CCl_4 complexes in n-hexane. For simple aromatics, these values are some two hundred times smaller than those found for the corresponding chloranil complexes.[5] However when aromatic solvents are used, quite large corrections are necessary to allow for the competition between solvent and donor.[6] Accordingly CCl_4 was chosen as the solvent in this work. It has the added advantage that the results obtained could be checked by an NMR method.

The method of obtaining the association constants relies heavily on the validity of the Benesi–Hildebrand relationship which in turn depends on compliance of the complexes with the Bouguer-Beer-Lambert Law. Also, the constants obtained are concentration constants (K_c). Since the activity coefficients are in most cases unknown and it is therefore important to work with as dilute solutions as possible (in this work the maximum concentration of donor and acceptor was 0.08 M though in most cases considerably less). Polle[7] has critically reviewed the method and Scott[8] has outlines an improved method for cases where the association constants are low.

Another assumption in the Benesi–Hildebrand approach is that the stoichiometry of the complex is 1:1. In order to verify this under our conditions, complex formation between 9-trimethylsilyltriptycene and TCNE was studied. Trimethylsilylation of triptycene[9] renders the molecule much more soluble in non-polar solvents and the triptycene residue itself could in principle complex with more than one molecule of TCNE.

The method of continuous variation was used and the resulting Job plot (Fig. 1) has a maximum at 1:1 stoichiometry and shows no detectable asymmetry, thus precluding the formation of higher order complexes.

The K_c values for a series of 9- and 9,10-substituted anthracenes with chloranil appear in Table 1 and the corresponding thermodynamic parameters in Table 2. The value of K_c for 9-t-butylanthracene could not be determined due to the solutions becoming rapidly opalescent on mixing. It is clear that the K_c values lie in a relatively small range. Substitution of bromine at the 9 position barely alters K_c and 9 methyl substitution shows an increase in K_c of less than a factor of two. From these results it seems that little charge has actually been transferred and that the complexes are rather better formulated as molecular complexes. Similarly the absence of any major steric effect is apparent since in the α alkylated series only small decreases occur and substitution by Me_3Si causes little if any change in K_c.

Table 1. Complex formation constants (K_c, l mole^{-1}) for Chloranil with anthracene derivatives at 25.0°

Donor	Solvent	K_c
Anthracene	CCl_4	3.1
Anthracene	$CHCl_3$.	1.7
Anthracene	CH_2Cl_2	1.0
9-Methyl-	CCl_4	5.6
9-Methyl-	CH_3CN	2.0
9-Ethyl-	CCl_4	5.5
9-Propyl-	CCl_4	3.8
9-i-Propyl-	CCl_4	2.4
9-i-Butyl-	CCl_4	3.5
9-Me_3Si-	CCl_4	2.8
9-Bromo-	CCl_4	2.4
9,10-Dibromo-	CCl_4	1.9
9,10-Dimethyl-	CCl_4	10.6

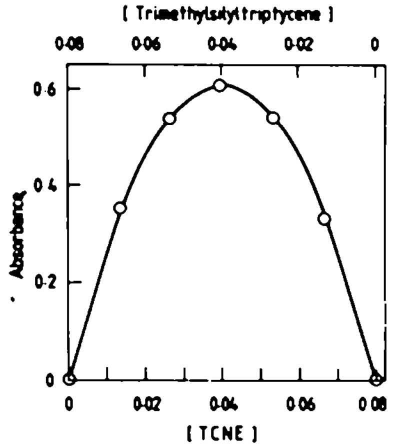

Fig. 1. Job plot (absorbance vs concentrations of trimethylsilyl triptycene and TCNE, mol l^{-1}) for complex formation in CH_2Cl_2 at 25°.

The entropies of formation lie in the range −8 to −11 e.u. with the exception of dimethylanthracene which has a significantly more negative value indicative of restricted rotation in the Me-group. The crystal structure of the 9-methylanthracene-chloranil complex has been reported.[10] The molecular planes of the two components lie parallel to one another at a separation of 3.45 Å. However, the chloranil does not lie symmetrically above the anthracene framework but is displaced towards one

Table 2. Thermodynamic parameters of complex formation of anthracene derivatives with chloranil in CCl_4 at 25.0°

Compound	$-\Delta G^{\circ}$ (cal.mole^{-1})	$-\Delta H^{\circ}$ (Kcal.mole^{-1})	$-\Delta S^{\circ}$ (cal.deg^{-1}mole^{-1})
1. Anthracene	672 ± 50	3.2 ± 0.4	8.6 ± 1.2
2. 9-Methyl-	1024 ± 33	4.3 ± 0.2	10.8 ± 0.5
3. 9-Ethyl-	982 ± 49	4.1 ± 0.2	10.4 ± 0.5
4. 9-Propyl-	792 ± 55	3.9 ± 0.3	10.4 ± 0.9
5. 9-i-Propyl-	546 ± 27	3.5 ± 0.2	9.8 ± 0.7
6. 9-i-Butyl-	744 ± 28	3.6 ± 0.5	9.7 ± 1.4
7. 9-Me_3Si-	662 ± 40	3.5 ± 0.3	9.4 ± 0.9
8. 9-Bromo-	529 ± 25	2.9 ± 0.2	8.1 ± 0.5
9. 9,10-Dibromo-	378 ± 35	2.8 ± 0.2	8.0 ± 0.8
10. 9,10-Dimethyl-	1399 ± 23	5.6 ± 0.1	14.0 ± 0.4
11. 9-Methyl-*	417 ± 40	3.2 ± 0.2	9.4 ± 0.5
12. Anthracene**	325 ± 50	2.7 ± 0.3	8.0 ± 0.8
13. Anthracene***	127 ± 50	2.7 ± 0.3	8.7 ± 0.8

* In acetonitrile; ** In $CHCl_3$; *** In CH_2Cl_2

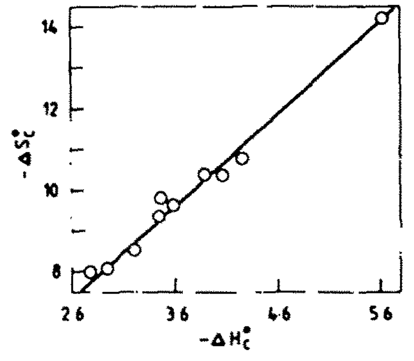

Fig. 2. Variation in ΔS_c° (cal deg^{-1} mole^{-1}) with ΔH_c° (kcal mole^{-1}) for the chloranil complexes with anthracene derivatives in CCl_4.

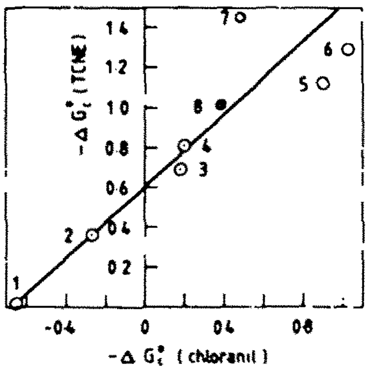

Fig. 3. Correlation of free energies of complex formation ΔG_c° (kcal mole^{-1}) for various aromatic compounds with TCNE and chloranil. See Table 4 for numbering.

of the outer rings with an angle of 1.5° between the plane normals. This suggests unfavourable interaction between CO and Me groups.

Plots of ΔH_c° vs ΔS_c° show a nearly linear correlation (Fig. 2). Such correlations have previously been found for complexes between iodine and aromatic hydrocarbons[11] and iodine and aliphatic amines.[12] However, Briegleb[13] has shown that for some groups of complexes having common acceptor species there is very little correlation. The data used however often relied on measurements taken at only *two* temperatures. The simplest interpretation of the correlation is that as the interaction between donor and acceptor becomes stronger (ΔH_c° more negative) there will be concurrently increasing constraints on vibrational modes in each component leading to a more unfavourable ΔS_c° term.

Correlations of stabilities of chloranil and TCNE complexes. Direct correlation in the anthracene series is not usually possible due to the paucity of data for TCNE which itself results from the generally high reactivity of the dienophile. Briegleb[5] has reported values† of ΔG_N°, ΔH_N° and ΔS_N° for a number of aromatic derivatives of varying structure using the two dienophiles in solvent CCl_4.

A plot of ΔG_c° (TCNE) vs ΔG_c° (chloranil) shows reasonable linearity for all derivatives except phenanthrene and triphenylene (Fig. 3). The slope of the line is close to unity and the following empirical relationship can be written

$$\Delta G_c^\circ\,(\text{TCNE}) = 0.91\,\Delta G_c^\circ\,(\text{chloranil}) - 0.60. \qquad (6)$$

Data for both dienophiles have been reported for 9-bromo, and 9,10-dibromoanthracene,[6] but only the dibromo derivative lies close to the above line. There are however examples where excellent linear relationships exist between data for two acceptors and a series of closely related donors. Fluoranil (F) and 1,3,5 trinitrobenzene (T) show such a correlation with alkylated benzenes where plots of log K_c(F) vs log K_c(T) give a straight line of slope 1.36.[1] Corresponding plots for chloranil and 1,3,5 trinitrobenzene give somewhat poorer correlations but a line of slope 1.31 was obtained.[1] It has been noted that whereas reasonably linear plots of log K_c vs Hammett σ values are obtained for electron donating substituents in the donor, the correlation breaks down when various electron-withdrawing groups are present.[14] It seems likely that in the latter series strong dipole-dipole interactions become dominant over charge-transfer interaction. In view of the sparse data for anthracenes it is tempting to construct a correlation based on the measured thermodynamic parameters for 9-bromo and 9-dibromoanthracene. However, in view of the anomalous behavior of electron withdrawing substituents it is by no means certain that these derivatives would be suitable models on which to base the desired correlations. Plots of ΔH_c° (TCNE) vs ΔH_c° (chloranil) are fairly linear but biphenyl and the two anthracene derivatives lie well off the line which has a slope of 0.51. The corresponding entropy correlations show quite a wide scatter. In view of the above difficulties it was decided to examine more indirect methods.

Correlations between $\bar{\nu}_{max}$, ionisation potentials and ΔG_c°. The excitation energy for transitions in charge-transfer complexes can be related to the ionisation potential of the donor and the electron affinity of the acceptor[15] and thus for a standard acceptor, $\bar{\nu}_{max}$ for the donor should be proportional to its ionisation potential (Ip). Briegleb and Czekalla[16] have found such relation-

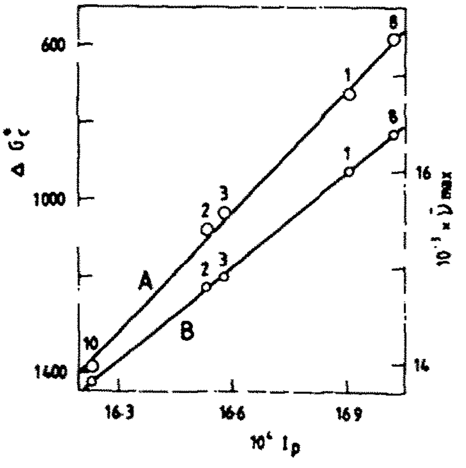

Fig. 4. Relationship between the ionisation potentials Ip(cal mole^{-1}) of anthracene derivative with (A) ΔG_c° for chloranil complexes and (B) the corresponding $\bar{\nu}_{max}$(cm^{-1}) in CCl_4 at 25°. Data taken from Table 3 and numbering from Table 2.

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†The equilibrium constants (K_N) were measured in mole fraction units. The corresponding K_c values can be calculated from the expression $K_N = 10.3\,K_c$. The corresponding thermodynamic parameters are related by the following equations

$$\Delta G_c^\circ = \Delta G_N^\circ + 1.36, \qquad \Delta H_c^\circ = \Delta H_N^\circ, \qquad \Delta S_c^\circ = \Delta S_N^\circ - 2.02.$$

Table 3. Correlation between ionisation potentials and $\bar{\nu}_{max}$ for various anthracenes

Compound	Ionization Potential[26] (e.v.)	$10^{-3} \times \bar{\nu}_{max}$(cm^{-1})
Anthracene	7.33 (169000)*	16.0
9-Methyl-	7.17 (165350)	14.8
9-Ethyl-	7.19 (165800)	14.9
9-Bromo-	7.38 (170190)	16.4
9,10-Dimethyl-	7.04 (162350)	13.8
9-Propyl-	-	15.0
9-i-Propyl-	-	15.3
9-i-Butyl-	-	15.2
9-t-Butyl-	-	15.2
9-Me_3Si-	-	15.7
9,10-Dibromo-	-	16.9

* The values in parentheses are in cal.mole^{-1}.

ships for complexes with iodine, 1,3,5-trinitrobenzene and chloranil. Five of the anthracenes in this study for which ionisation potentials are available show a similar linear dependence (Fig. 4) Table 3, yielding the relationship

$$\bar{\nu}_{max} = 7640\,Ip - 40{,}000 \qquad (7)$$

which can be rewritten in terms of energy

$$E = 0.947\,Ip - 4.96 \qquad (8)$$

where Ip is in eV. Plots of ΔG_c° vs Ip also give a good straight line correlation (Fig. 4) which can be used for predicting either of the quantities for a given member of the anthracene series.

Although measurements of ΔG_c° for TCNE complexes are very difficult for anthracenes, values of $\bar{\nu}_{max}$ are available and when plotted against the corresponding values for chloranil give an extremely good linear correlation whose slope is almost unity. (Table 4, Fig. 5)

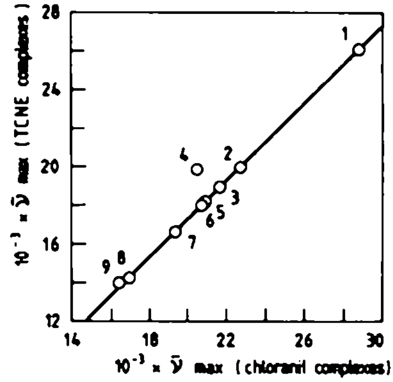

Fig. 5. Relationship between wave-number ($\bar{\nu}_{max}$ cm^{-1}) of the charge-transfer band of TCNE and chloranil complexes with some common donors (see Table 4 for numbering).

Table 4. $\bar{\nu}_{max}$ (cm^{-1}) of charge-transfer band for TCNE and chloranil with some donors in carbontetrachloride[27]

Compound	$10^{-3}\ \bar{\nu}_{max}$	
Donor	Chloranil	TCNE
1. Benzene	28.8	26.1
2. Diphenyl	22.7	20.0
3. Phenantherene	21.6	19.0
4. Durene	20.5	19.9
5. Naphthalene	20.9	18.2
6. Triphenylene	20.7	18.0
7. Stilbene	19.4	16.6
8. 9-Bromoanthracene*	16.4	14.0
9. 9,10-Dibromoanthracene*	16.9	14.3

* This work

yielding the empirical equation

$$\bar{\nu}_{max}\,(\text{TCNE}) = 0.993\,\bar{\nu}_{max}\,(\text{chloranil}) - 2520 \qquad (9)$$

where $\bar{\nu}_{max}$ is in cm^{-1}. The only donor molecule which lies off the above line is durene which is likely to show some steric hindrance to complexation. A plot of ΔG_c° vs $\bar{\nu}_{max}$ for chloranil complexes gives a reasonably good straight line correlation provided the substituents at the 9 position are not too bulky (Fig. 6). Thus by using the calculated ν_{max} for TCNE from eqn (9), values of ΔG_c° for this reagent can be determined. These results appear in Table 5. A simpler, though less accurate approach is to add to ΔG_c° (chloranil) the average difference between the free energies for 9-bromo and 9,10-dibromo anthracenes (for chloranil and TCNE), taking data from Ref. 6 and Table 2 (Table 5).

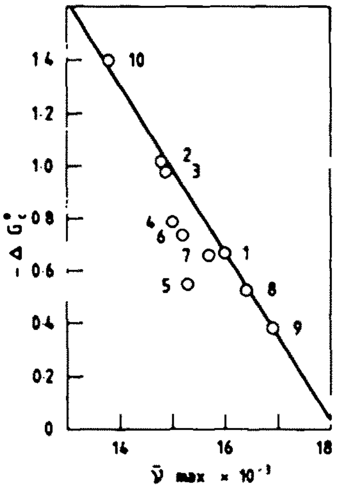

Fig. 6. Plot of ΔG_c° (kcal mole^{-1}) against $\bar{\nu}_{max}$(cm^{-1}) for chloranil complexes with anthracene derivatives (see Table 2 for numbering).

Finally, a good correlation exists between ΔG_c° for TCNE and the ionisation potentials of the aromatic donors (Fig. 7). The data used to establish this plot were drawn from Refs. 6, 17 and 18 (Table 6).

This resulted in the empirical relationship

$$\Delta G_c^\circ = 0.0414\,\text{Ip} - 8525 \qquad (10)$$

where Ip is in cal mole^{-1}. For donors where the ionisation potential is not known $\bar{\nu}_{max}$ is measured or estimated from eqn (9) and ΔG_c° calculated using eqns (7) and (10). The results of all the methods used are compiled in Table 5. The agreement is good and the values can be relied upon with some confidence. In addition, it

Table 5. Calculated free energies (ΔG_c°, kcal mole^{-1}), entropies (ΔS_c°, cal deg^{-1} mole^{-1}) and equilibrium constants (K_c l mole^{-1}) for complex formation between 9-substituted anthracenes (9-X-AnH) and TCNE in CCl_4 at 25°

	$-\Delta G^\circ_c$					
X	a	b	c [g]	d	$-\Delta S^\circ_c$ [e]	K_c [f]
H	1.52	1.5	1.5	1.2	5.6	13
Me	1.68	1.8	1.9	1.5	8.8	18
Et	1.66	1.8	1.8	1.5	8.2	18
Pr	1.65	1.6	(1.8)	1.3	7.6	18
iPr	1.61	1.4	(1.7)	1.1	6.3	15
tBu	1.62	-	1.7	-	-	15
iBu	1.62	1.5	(1.7)	1.3	6.3	15
Me_3Si	1.56	1.5	1.6	1.2	6.5	15
Br	1.48	1.3	1.4	1.1	4.8	13
9,10-Br_2	1.41	1.2	1.2	1.0	4.7	11
9,10-Me_2	1.80	2.2	2.2	1.8	4.7	21

a - calculated from eqns. (7) and (10)

b - calculated from average difference between values of ΔG°_c for TCNE and chloranil from data for 9-bromo and 9,10-dibromoanthracene (ref. 6 and present work. Errors ±0.3 k.cals.mole^{-1})

c - calculated from eqn. (9) and using the $\bar{\nu}_{max}$, ΔG°_c correlation

d - calculated from eqn. (6)

e - calculated from ΔG°_c values, assuming that ΔH°_c (TCNE) = ΔH°_c (chloranil)

f From $\Delta G^\circ_c = -RT\ln K_c$ using data in column a

g The values appear in parenthesis since these substituents lie off the $\bar{\nu}_{max}$, ΔG°_c correlation

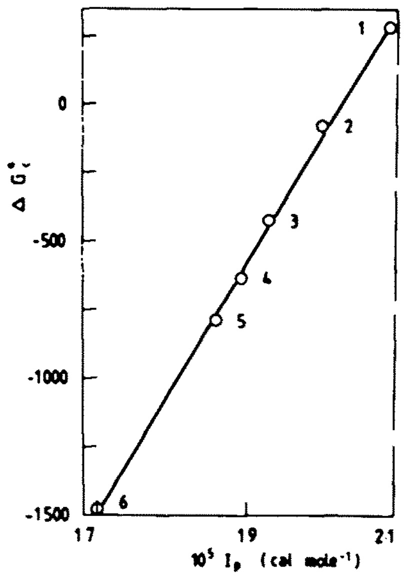

Fig. 7. Relationship between ΔG_c° (cal mole^{-1}) and ionisation potential Ip (cal mole^{-1}) for aromatic compounds with TCNE in CCl_4 at 25° (numbered as in Table 6).

Table 6. Free energies of TCNE complexes at 25.0° in carbontetrachloride with the ionization potentials of some aromatic donors

Donor	I.P.[17] (e.v.)*	ΔG°(cal.mole^{-1})**
1. Benzene	9.24	282
2. Toluene	8.82	-81
3. 1,4-Dimethylbenzene	8.48	-422
4. Naphthalene	8.3	-634
5. 1,3,5-Methylbenzene	8.14	-792
6. 9-Bromoanthracene	7.38	-1480***

* 1 e.v. = 96487.0 J = 23060.9 cal.mole^{-1}

** From reference 18

*** From reference 6

was noted that values of ΔH_c° for chloranil and TCNE for 9-bromo and 9,10-dibromoanthracene were the same within experimental error. If one assumes that this occurs for the other anthracene derivatives then ΔS_c° can be estimated in the usual manner. The results appear in Table 5 and are remarkable for their relatively small variation, complex formation clearly is not very sensitive to the nature of the 9 substituents.

Of particular interest is the value for 9,10-dimethylanthracene which is considerably less negative than the corresponding value for chloranil. This could reflect the greater steric compressions between the Me groups at C9 and C10 and the CO groups in the dienophile. The results can now be used to examine in more detail the mechanism of Diels–Alder additions of TCNE to anthracene derivatives, reports of which appear in the following papers. Solvents effects on complex formation will also be dealt with in a subsequent paper.

EXPERIMENTAL

Purification of solvents and reagents. AR grade $CHCl_3$ was washed four times with an equal volume of water and dried over $CaSO_4$. The solvent was freshly distilled immediately prior to use. Dichloromethane was similarly purified. Fison's spectrograde CCl_4 was used without further purification.

TCNE was recrystallised from benzene and twice sublimed at 120° under 4 mm Hg m.p. 198–200°. Chloranil was recrystallised from benzene and sublimed at 130–140° under 1 mm Hg to give yellow needles m.p. 288–290°. Anthracene (BDH, blue fluorescent) was chromatographed on alumina and then recrystallised from EtOH, m.p. 218–219°.

Preparation of anthracene derivatives. The 9-ethyl derivs were obtained by reaction of the relevant alkylmagnesium halide with anthrone,[19] with a modification for 9-t-butylanthracene.[20]

9,10-*Dimethylanthracene.*[21] 9,10-bis(Chloromethyl)anthracene (I) was prepared by the method of Miller *et al.*[22] It is a *severe* skin irritant and should be handled with great care. A soln of I (1.38 g, 5 m mole) in DMSO (25 ml) was mixed with $NaBH_4$ (0.8 g, 22 m mole). The mixture was heated at 100° for 1 hr with stirring, cooled in ice and distilled water (50 ml) added. The resulting yellow ppt was filtered off and recrystallised from benzene to give 1.0 g (97%) bright yellow needles, m.p. 181–183°.

9-Bromo,[23] 9,10-dibromo[24] and 9-trimethylsilylanthracene[25] were prepared by standard procedures. 9-Trimethylsilyltriptycene was synthesised by benzyne addition to the corresponding anthracene.[9]

Determination of K_c. A Unicam SP 1700 UV-visible spectrophotometer was used throughout the work. Constant temps. (±0.1°) were maintained using a Churchill thermocirculator. The absorbances of the solns were obtained by direct digital read-out.

A stock soln of chloranil in CCl_4 was made up and added to various weights of the anthracene derivatives in 10 ml volumetric flasks, then made up to the mark with solvent. 3 ml aliquots of these solns were placed in 1 cm silica cuvettes, placed in the cell housing and allowed to equilibrate for 30 min before the absorption was measured.

Table 7 lists the values of λ_{max} at which readings were taken for the various anthracenes.

The equilibrium constants, K_c(l mole^{-1}) were calculated from the Benesi–Hildebrand eqn (11)

$$\frac{[\text{choranil}]}{A_e} = \frac{1}{K_c\,\epsilon[\text{anthracene}]} + \frac{1}{\epsilon} \tag{11}$$

by plotting the LHS of (11) vs [anthracene]$^{-1}$. At least five different anthracene concentrations were used and each set of data was repeated with

$$\frac{[\text{anthracene}]}{(\text{chloranil}]} \geq 30.$$

Table 7. Analytical wavelengths (ν_{max} n.m.) used in the evaluation of K_c for complexes of anthracenes with chloranil in CCl_4

	Compound	ν_{max}
	Anthracene	625
9-Me	"	675
9-Et	"	670
9-Pr	"	665
9-iPr	"	655
9-tBu*	"	660
9-iBu	"	660
9-Me$_3$Si	"	635
9-Br	"	610
9,10-dibromo	"	590
9,10-dimethyl	"	725

* Solutions were opalescent

Table 8. Values of K_c (l mole^{-1}) for anthracene derivatives with chloranil in CCl_4 at various temperatures

Compound	Temp	K_c	Compound	Temp	K_c
Anthracene	20.2	3.4	9-1 butyl "	25.0	3.5
"	25.0	3.1	" "	29.4	3.3
"	33.9	2.6	" "	40.5	2.6
"	41.5	2.3	" "	50.6	2.1
9-methyl "	25.0	5.6	9-Me_3Si "	25.0	3.0
" "	35.0	4.5	" "	34.7	2.5
" "	48.6	3.3	" "	50.5	1.9
9-ethyl "	20.1	5.5	9-bromo "	20.7	2.8
" "	32.1	4.0	" "	28.7	2.5
" "	41.9	3.3	" "	35.2	2.3
" "	49.1	2.9	" "	43.4	1.9
9-propyl "	22.6	4.0	9,10 dimethylanthracene	22.6	11.4
" "	30.2	3.3	" "	33.2	8.3
" "	40.0	2.7	" "	42.1	6.5
" "	48.9	2.3	" "	49.4	5.2
9 i Propyl "	20.9	2.6	9,10 dibromo "	21.2	2.0
" "	29.4	2.2	" "	31.1	1.7
" "	40.4	1.8	" "	41.9	1.5
" "	47.4	1.6			

The best line and intercept were obtained by multiple regression analysis using an interactive data analysis programme (K. I. McDonald, University of Essex).

Values of K_c were reproducible to within ±5%.

The thermodynamic parameters were obtained from data at a minimum of four different temps and evaluated from the Van' t Hoff relationship using a least squares computer programme.

Table 8 lists the data used.

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